

"EXPRESS MAIL" MAILING LABEL
NUMBER: EK431422203US
DATE OF DEPOSIT: March 23, 2000
I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE
UNITED STATES POSTAL SERVICES "EXPRESS MAIL POST OFFICE TO
ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED ABOVE
AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS,
WASHINGTON, D.C. 20231
TRICIA E. VAN HOOSER
(typed or printed name of person mailing paper or fee)
Tricia E. Van Hooser
(signature of person mailing paper or fee)

Additive for Wellbore Fluids

- 5 This invention relates to an additive for wellbore fluids. More specifically, it pertains to an additive for modifying the properties of a filtercake formed at the boundary between wellbore and formation.

BACKGROUND OF THE INVENTION

- 10 For the production of hydrocarbon wells, boreholes are drilled into subterranean formations. Following standard procedures, a fluid is circulated during drilling from the surface through the interior of the drill string and the annulus between drill string and formation. The drill fluid also referred to as drilling mud is used to lubricate the drill bit. It also balances the formation pressure so as to prevent formation fluids to enter the
15 borehole in an uncontrolled manner.

- The industry distinguishes between largely three classes of drilling fluids: oil-based, water-based and so-called synthetic muds. Whereas oil-based muds are recognized for their superior qualities for most of the drilling operations themselves, they become
20 increasingly undesirable due to their impact on the environment and stricter environmental legislation. Water-based muds are expected to replace oil-based mud as the drilling fluid of choice in major geographical areas.

Other fluid systems used in the oilfield industry are completion and workover fluids. By definition a completion or workover fluid is a fluid that is placed against the producing formation while conducting such operations as well killing, cleaning out, drilling in, plugging back, controlling sand, or perforating. Basic fluid functions are to facilitate
5 movement of treating fluids to a particular point downhole, to remove solids from the well, and to control formation pressures.

Required fluid properties vary depending on the operation, but the possibility of formation damage is always an important concern. In recent years many new fluid
10 systems have appeared, most due to the recognition of the high risk of reducing the productivity, or completely plugging certain sections of the producing zone, through contact with a foreign fluid.

A wellbore fluid typically contains a number of additives. Those additives impart desired
15 properties to the fluid, such as viscosity or density. One class of additives is used as fluid loss agents to prevent the drilling fluid from entering into porous formations.

The basic mechanism of fluid loss control is generally the formation of a filtercake at the interface of the porous or permeable formation layers. As part of the drilling fluid is
20 forced into the formation by the higher pressure within the wellbore, larger particles and additives are left behind and accumulate at the face of the formation. The filtercake thus formed can be regarded as a membrane that protects the formation from further invasion of wellbore fluids. Fluid-loss control agents are selected in view of their quality to form a competent filtercake.

25 High molecular weight, oil soluble additives have been widely used as diverting agents and in water based drilling and completion fluids. The additives help build an effective filtercake at the formation face and minimize damage. Under flowback conditions, the reservoir hydrocarbons readily dissolve the additive effectively creating holes in the

filtercake and aiding formation cleanup. Having a hydrocarbon-induced breakdown of the filtercake avoids chemical intervention (clean-up) and hence can result in a very cost-effective method of drilling wells for hydrocarbon production.

- 5 Many different oil soluble additives can be used to control fluid loss. High molecular weight thermoplastic hydrocarbon resins are commonly used. United States Patent Nos 3,891,566 and 3,827,498 describe for example a mixture of two oil soluble resins, one being friable and the other pliable as fluid loss control agents and as diverting agents. The resin must be used where oil exists and therefore it cannot be used in dry gas wells or in
10 wells with temperature above its softening point. Its high molecular weight and impurities can make it only partially soluble in hydrocarbons causing the residues to damage or block the formation.

- It is therefore an object of the present invention to provide a novel class of fluid loss
15 additives that are able to form a competent filtercake while being easily removable from hydrocarbon bearing formations.

SUMMARY OF THE INVENTION

- 20 According to one aspect of the present invention, there is provided a low molecular weight, high melting point, crystalline, oil soluble additive for use in wellbore fluids that include drilling, completion, workover, fracturing, acidizing, cementing fluids and the like.
- 25 The new additive is a wellbore-fluid additive which is preferably a ground crystalline material of melting point over 80°C, preferably over 100°C which is readily soluble in produced hydrocarbons such as crude oil and lighter condensates, and which exhibits a molecular weight of less than 1000, and preferably less than 650.

Its particle size can be adjusted to bridge efficiently across different pore size formations and control its solubility rate. A preferred particle size range is 10000 to 1 micron.

- 5 Preferred examples of the low molecular weight crystalline additives are 1S-endo-Borneol, camphor or iodine. Other examples include beta carotene with a melting point of 184 degrees Celsius and a molecular weight of 537, lycopene (175; 537), cholesterol (150; 387), lanosterol (139; 426), and agnosterol (165; 424). More preferred examples are Woolwax alcohols distillation residues (Lanolin wax), a derivative of wool grease
- 10 comprised of high molecular alcohols (triterpene, aliphatic etc) and fatty acids (normal, isoacids etc) with melting point of 90 degrees Celsius and a molecular weight of approximately 425.

- The invention reduces formation damage, flow initiation pressure, and increases the
- 15 cleanup efficiency dependent on the formation type. Compared to other additives, the low molecular weight crystalline additive can provide some important advantages. Firstly, the conventional high molecular weight resins, during the initial stages of dissolution in produced hydrocarbons, can be plasticized by the oil to a tacky material. This tends to coalesce to a sticky mass and is very difficult to remove by dissolution. Secondly, the
- 20 pressure required to start the backflow of oil through such filtercake can be high and therefore the resins have limited use in wells with low drawdown pressures. Thirdly, the level of impurities in the hydrocarbon resin can limit its cleanup. By contrast, the low molecular weight crystalline solids of this invention dissolve smoothly and quickly to give low viscosity solutions.

25

In a variant of the invention, it is envisaged to reduce the environmental hazards and nuisance caused by some of the new crystalline solids compounds by an encapsulating treatment.

Another aspect of the invention relates to using the novel additive as part of a well operation. Such application comprises the steps of injecting a wellbore fluid with the additive, letting the additive form a filter cake, reversing the flow by changing the wellbore pressure and dissolving the additive in the filtercake through the flowback of hydrocarbon from the formation.

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the fluid loss behavior of a drilling fluid dependent on the additive particle size and sequential fluid using Borneol;

FIG. 2 shows the fluid loss behavior of a drilling fluid dependent on the additive particle size and sequential fluid using Lanolin; and

FIG. 3 summarizes steps of method to apply the novel additive in a subterranean well operation.

MODE(S) FOR CARRYING OUT THE INVENTION

Using 1S—endo-Borneol ($C_{10}H_{18}O$) having a molecular weight of 154 and melting point of $210^{\circ}C$ ($410^{\circ}F$), it was first bottle tested for its solubility in water, kerosene and kerosene with 5% mesitylene (aromatics) at $25^{\circ}C$. 2 g of the additive added to 50 ml of the test fluid was insoluble in water but dissolved completely, within 5 minutes of mixing

in kerosene and kerosene with mesitylene. There was no evidence of any residues in both cases. The additive was insoluble in water at higher temperature of 80 °C.

Tests were then performed to demonstrate the ability of this additive to increase the permeability of a drilling fluid filtercake when contacted with kerosene. A 2.5 inch diameter High Pressure-High Temperature filtration cell was used for the tests. Sequential static filtration tests were performed on a filter paper (2 micron pores) at 100 psi pressure and 25 °C temperature using the polymer/carbonate drilling fluid containing 10 ppb of the crystalline additive followed with kerosene. The composition of the drilling fluid is given in Table 1.

Table 1: Composition of a polymer/carbonate drilling fluid.

	lb/bbl	gl ⁻¹
CaCl ₂ (74g in 835 ml of H ₂ O)	346	986
Antifoam	0.2	0.6
Starch	6.0	17.1
Scleroglucan	1.5	4.3
Biocide	0.1	0.3
Calcium carbonate	45.0	128.3

The effect of varying the particle size of the additive (d_{50} of 400, 200, and 60 microns) was investigated. Care was taken not to disturb the filtercake when emptying the residual mud from the cell and introducing kerosene.

- 5 FIG. 1 shows the fluid loss behavior with elapsed time. After the mud cake build-up period of one hour, the kerosene dissolves the additive in the filtercake and increases its permeability to an extent that is particle size dependent. The strongest effect was observed with approximate particle size of 400 micron. But even 200 micron samples and 60 microns samples resulted in a much increased permeability. In the case of a fine grade
10 the permeability increases by as much as 60 times whereas in the control test without the additive the rate increases by only 6 times.

- Filtercake examined at the end of the test showed pinholes distributed uniformly over the entire surface due to the dissolved additive whereas in the control test the pinholes were
15 absent.

- When water is flowed instead of kerosene through a drilling fluid filtercake containing 60-micron size additive there is no change in permeability, further demonstrating the efficient removal of the additive with kerosene.
20

- To illustrate the ability of the present invention to reduce fluid loss, formation damage and initial backflow pressure, tests were run in a High Pressure – High Temperature cell adapted for cores. The cores were 25.4 mm in diameter and 30 mm in length. Three outcrop cores (Ketton limestone, Clashach sandstone and Birchover sandstone) of widely
25 different permeability and pore size were used. Their permeability was approximately 2400 mdarcy, 850 mdarcy and 10 mdarcy, respectively and median pore size was 60 μ m, 33 μ m and 2 μ m, respectively. The cores were first vacuum saturated in brine (45 gl^{-1} NaCl and 5 gl^{-1} CaCl_2) and then flushed with kerosene to residual water saturation. The initial permeability to kerosene was determined from the measured steady state pressure drop

across the rock corresponding to the imposed range of constant flowrates (10, 8, 6, 4, and 2 ml min⁻¹). The flowrates used for Birchover was 5 times lower.

Static filtration tests were conducted for 4 hours at 300 psi differential pressure and 25 °C
5 temperature using polymer/calcium carbonate drilling fluid containing 10 ppb of 60
micron additive (in the opposite direction to the kerosene flood). After filtration the cell
was depressurised and a backflow of kerosene was imposed at 1 ml min⁻¹ to measure the
peak (FIP or flow initiation pressure) and steady state flow pressure. The peak pressure
correlates with the rupture of the filtercake. The final permeability was measured using
10 the same procedure as used for the initial permeability. The retained permeability was
defined as the ratio of final to initial permeability in percentage.

As shown in Table 2, the additive gave a two-fold increase in the retained permeability
and reduced the spurt loss, fluid loss and FIP in the case of large pore size Ketton. The
15 spurt loss was higher compared with the other two rocks of smaller pore size resulting in
an internal filter cake. The cleanup of this internal cake was promoted by the presence of
the additive resulting in a higher retained permeability and lower FIP.

In contrast, an external filter cake was mainly built on the smaller pore size rocks. With
little or no internal cake, the additive contributed little to the retained permeability.
20 However, the external filtercake with the additive was made more easily permeable
indicated by a lower FIP by as much as 2 times in the case of Birchover sandstone.

TABLE 2

Rock type	Drilling Fluid + / - Additive	Fluid loss at 4 hr g	Initial and final perme ability mdarcy	Spurt loss g	Retained Permeability %	FIP psi
Ketton	-	2.4	2619 / 767	0.63	29	5.5
"	-	2.4	4817 / 929	0.78	20	8.0
"	+	1.8	2114 / 1276	0.47	60	3.0
"	+	1.6	2411 / 1647	0.41	68	2.1
Clashach	-	1.4	999 / 572	0.15	77	5.2
"	+	1.2	705 / 540	0.11	77	5.0
Birchover	-	1.5	7.2 / 6.8	0.06	92	76
"	+	1.3	11.7 / 10.2	0.06	87	41

- 5 For an encapsulating treatment Borneol particles can be ground to an average particle size of 60 microns. Then, the particles can be spray coated using Piccopale 85-55KX oil soluble resin. The resulting coating is nominally 0.1 microns thick. These particles are then added to a typical reservoir water based drilling fluid (composition same as other examples).

10

An further example used is lanolin wax. Its solubility in kerosene and water was qualitatively investigated by performing bottle tests at 60 degrees Celsius. Granulated lanolin with a maximum size of 500 microns dissolved completely in kerosene within 20 minutes of mixing, while being insoluble in water.

15

Tests were performed to demonstrate the ability of lanolin to increase the permeability of a drilling fluid filtercake (polymer/carbonate) when contacted with kerosene. Sequential filtration tests were performed with the lanolin additive in drilling fluid followed by kerosene and the fluid loss was monitored with time. Two grade sizes (500-200 microns and 60-200 microns) of lanolin was investigated. The tests were performed on a filter paper at 100 psi differential pressure and 25 C following the procedure described above. The control test was without the additive.

FIG. 2 shows a respective 15 and 35 fold increase in fluid loss after contacting kerosene with the filtercake containing the two grades of lanolin. However, the control test without added lanolin showed no significant increase in fluid loss.

FIG. 3 summarizes important steps for applying the additive in a well operation. The steps can be embedded for example in a drilling operation or other operation requiring the formation and later breaking of a competent filtercake at the face of permeable subterranean formation layers.